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TECHNICAL INFORMATION SERIES

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Title Page		
AUTHOR	SUBJECT CLASSIFICATION	NO.
R.E. Plump T. W. Liao	Gaseous Insulation	57TP517
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Progress in Gaseous Insulation		

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GENERAL ELECTRIC

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AUTHOR R.E. Plump T. W. Liao		SUBJECT CLASSIFICATION Gaseous Insulation	NO. 57TP517 DATE 2/14/58
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ABSTRACT Theoretical, experimental, and practical developments in gaseous dielectric phenomena are reviewed from recent literature. Chemical and physical properties of gases and their effects, are also discussed. (113 references.) The report was originally written for Heywood & Co. of London as a chapter for a book on Progress in Dielectrics.			
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CONCLUSION Interest in gaseous insulation is world-wide, and much progress has been made in the past decade. Areas in this field include rotating machinery, power apparatus, switchgear, cables, etc. Theoretical and experimental advances have been made toward more understanding of the requirements of particular applications. A distinction between electronegative gases and all others appears to be firmly established. Lighter gases such as hydrogen and helium still retain much usefulness for heat transfer in rotating machinery, but the chemistry and physics of heavier gases are favorable for many other applications.			

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Progress in Gaseous Dielectrics

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1. Introduction

The field of gaseous dielectric phenomena has expanded greatly in the past ten years, - not only has the world's knowledge of the subject increased in scope but also in precise detail. Electrodes have been immersed in gases at pressures from 10^{-5} to 10^{-5} centimeters of mercury, and the electrical properties of the systems have been described. The type of gas studied has increased in complexity from helium to perfluoromethylcyclohexane, and the electrical equipment for the purpose may have consisted of a simple d.c. voltage circuit or a complicated wave guide apparatus. Some men have been primarily interested in molecular cross-sections, while others have striven to adapt a specific gas to commercial usage. This complexity and its necessary detail are indicated by the number and variety of publications across the world. For our part, we shall lean most strongly on the activities which have a semblance of practicality, much as the word may be abhorred.

We shall not ignore the abstract or theoretical, however, for without them there is no understanding, and understanding is also practical. The possible reasons why one gas differs from another in dielectric behavior, for example, provide a basis from which to estimate the probable characteristics of a new gas. Varying molecular composition most certainly is reflected in the breakdown results of different gases. Similarly, electrode configurations may have an effect on the behavior of a given gas, and this also should be understood.

Progress, therefore, comprises not only approaching the goal of utilizing insulating gases, but also a gain in our knowledge of what the gases do, what they are composed of, and what affects them.

1.1 The Desirable Properties of Gases for Practical Use

As a greater versatility of operating performance is demanded of an insulating gas, the more limited are the properties which the gas must embody. This versatility, so desirable in being able to meet any adverse situation, is non-existent in a majority of gases because their characteristic properties fall short of meeting an imposed wide range of operating conditions. The property of condensing as a liquid from the gas phase at a certain pressure and temperature can be used as an example. If the equipment exposed to wintry conditions is to function normally, the insulating gas should not be effectively removed from service by draining to the bottom as a liquid. Similarly, an otherwise excellent gas, if it is chemically reactive to a vital part made of an indispensable material, might be considered only for a short-time use. Such a situation can arise, of course, and it is somewhat analogous to using a very expensive gas in small quantities per unit of apparatus, making the cost in both instances well worth the advantage. When hundred or thousands of pounds of gas are concerned, however, the cost becomes an important item and other characteristics, such as recoverability and chemical inertness, also assume greater significance.

Preferred properties in a gas are:

- (a) High dielectric strength,
- (b) Thermal stability and chemical inactivity toward all materials of construction,
- (c) Non-flammability,
- (d) Physiological inertness,
- (e) A low temperature of condensation,
- (f) Good heat transfer, and
- (g) Ready availability at moderate cost.

These are most of the desirable characteristics of a utilitarian gas, and the above order of listing after (a) (which is probably of primary concern) need not be necessarily according to relative importance. For special uses, other properties such as a low viscosity or perhaps an easy attainment of high purity and adequate maintenance may be of dominant interest. Nevertheless, a gas for electrical purposes meeting most or all of the above requirements should be preferred. Intelligent compromise, and concessions to existing properties of materials leading to new adaptations of apparatus are common and a strong survival pattern in the electrical industry. Recent experience has shown that employing any known gas will entail adjustments in design for best use. This is true for sulfur hexafluoride which has received much study and has been found to possess most of the above requirements. Better gases probably exist or can be found, and the search continues.

1.2 Mixtures

A combination of two or more gases for a single purpose is of course a logical line to pursue when one gas does not contain all the necessary attributes. In accordance with physical chemistry, much can be accomplished through an understanding of partial pressures. For example, the condensation point is a function of the partial pressure of a gas in a mixture and is related to the liquid-vapor pressure curve of the pure substance. An effective total pressure of the system will be very close to the sum of all the partial pressures. However, the effect of mixing two or more gases on the resulting electrical properties has only rather narrowly been studied.

One of the qualitative effects of mixing has been the elevation of dielectric strength, or simply the prevention of corona at desired operating voltages. Joliot et al¹ observed the latter effect on air containing vapors of carbon tetrachloride, and in the same year the striking photographs of Nakaya and Yamasaki² appeared, showing for example, a strong "smoothing" of sparks in air containing less than one volume percent of chloroform. These authors referred to Terada³ et al as being the first to see this effect. Later, Skilling and Brenner⁴ published their systematic results on mixtures of CCl_2F_2 and N_2 showing abnormally large gains in dielectric strength when less than 5 percent by volume of the Freon was added.

2. Theoretical and Experimental Advances

2.1 Early Developments

The observation of electrically ionized gas is as old as Man. His use of fire unknowingly involved the production of charged gases. But from a materialistic standpoint, the study of a variety of gases only began in 1887 when Thomson⁵ delivered the Bakerian Lecture on the dissociation of iodine, bromine, chlorine, and nitrogen tetroxide, by the spark from an induction coil. Two years later Natterer⁶ reported a similar but greatly extended study on some twenty-five inorganic elements and compounds, and twenty-nine organic compounds including such diverse

gases as carbon monoxide, hydrogen cyanide, acetylene, ethane, benzene, carbon tetrachloride, ethyl acetate, and diethyl mercury at 25 mm. pressure and at atmospheric pressure. Perhaps even more surprising, the list of inorganic substances included phosphine, tin tetrachloride, arsenic trichloride, and mercuric chloride at temperatures up to 330°C. Natterer not only measured the maximum spark distances a gas could support, and the length of glow on the negative wires at the reduced pressure, but also the distance from the spark at which he could read a book in the darkened room. This type of interest in large material variety again appeared only many years later in the reports of Charlton and Cooper⁷ and of Thornton⁸.

⁹ The first report on sulfur hexafluoride appeared in 1900 when Berthelot, having received about 30 c.c. of perfluoride of sulfur from M. Moissan, found no volume change and no chemical reactivity toward bromine, acidic cuprous chloride, or thiophene, after 4 hours of induction coil sparking. The interior of the tube showed evidence of reaction which Berthelot attributed to impurities in the gas, perhaps. He concluded that the perfluoride of sulfur was comparable with the fluorides of boron and silicon in stability. Not until thirty-eight years later Goldstein¹⁰ published an ionization potential of 19.3 e.v. for SF₆ and in the same year Pollock and Cooper¹¹ included this gas in a systematic study of pressure effects on a positive point. All of these people evidently possessed a strong interest in material substances.

Historically, it is interesting as a coincidence that Paschen¹² became the father, perhaps, of the mechanistic interest in electrical breakdown in the same publication year as Natterer. Paschen is remembered today for the results in his doctoral dissertation at the University of Strassburg. With three different gases, hydrogen, carbon dioxide, and air, he demonstrated an inter-dependence of gas pressure and gap distance, relating the product to a characteristic breakdown voltage. It should be noted here also that Max Wolf, in the same volume, pages 306-315, gave electrical breakdown data for air, oxygen, carbon dioxide, and nitrogen in a 0.1 cm. gap at pressures up to 5 atmospheres, and for hydrogen up to 9 atmospheres. Plotting the breakdown strengths against increasing pressure gave straight line proportionality. This is probably the first experiment on gaseous breakdown performed at relatively high pressures.

Broadly speaking, electrical breakdown of gases can be described as the transition from an insulating to a conducting state. An insulating gas has a very low conductivity resulting from relatively few electrons and positive and negative ions. For instance, ordinary air has only a few hundred positive and negative ions per cubic centimeter. This number can be increased many thousand times by heating the gas or by irradiation with a radioactive source. However, to reach a conducting state, the ion pairs must be multiplied by at least 10¹⁵ times or so. This can only be efficiently produced by an ionization process in which the free electrons are accelerated by an applied electric field to energies that are high enough to produce ion pairs from the nearby gas molecules. The electrons thus produced are similarly accelerated to produce more ion pairs resulting in a chain reaction. The rate of ion production by this so-called

"ionization-by-collision" process was experimentally determined by Townsend¹³ who found that the electronic current (J) could be expressed by an equation,

$$J = J_0 e^{\alpha d}$$

where d is the distance between two uniform field electrodes and α is known as Townsend's First Coefficient.

The coefficient α depends upon the electric field for a given gas at a given pressure. The relationship can be evaluated experimentally for various values of the applied field strength. For instance, such a relationship for air has been given by Sanders^{14, 15} as shown in Table I.

Townsend found that although a large number of ion pairs could be produced at the end of each filament of ionization or discharge, no complete electrical breakdown would occur unless at least an additional free electron was produced by a secondary process at the origin of each discharge. The breakdown criterion was then expressed as

$$\gamma(e^{\alpha d} - 1) = 1$$

where γ is the Townsend's second coefficient.

The mechanism associated with the first coefficient is described as ionization by collision whereas that associated with the second coefficient is more complicated. There are three possible mechanisms responsible for the generation of the secondary electrons; each may prevail under a different breakdown condition. The secondary electrons may be produced at the cathode by bombardment of the returning positive ions, as in the case of a glow discharge. They may emit from the cathode by photoelectric action as a result of the excitation and recombination processes in the discharge. These may be termed as Townsend type breakdown where the electric field is at the threshold of breakdown. Finally, the secondary electrons may be generated by photoionization in the gas by the intensified field near the discharge resulting in streamer type discharges and branching of the original discharge. This phenomenon often occurs at fields over the threshold for breakdown.

The experimental evaluation of the second coefficient is more complicated than that of the first coefficient. The values for air¹⁶, as shown in Table II, illustrate that its value does not increase consistently with E/p as in the case of the first coefficient.

The above review is an oversimplified picture of the mechanistic processes of gas breakdown. The intent is not to specify conditions under which a certain type of breakdown may take place. It is rather to serve as an introduction for bringing in some recent progress in the line of such a picture.

2.2 Some Recent Progress

Because of the voluminous publications on both theoretical and experimental contributions to gas breakdown, a full treatment of the entire subject is not intended here. An excellent and extensive treatise of the entire subject of gas discharge is given in several recent publications.^{17, 18, 19, 20} In the majority of these publications, the discussion pertains to simple gases rather than polyatomic ones and breakdown mechanisms rather than electric strength evaluations. Since this article is inclined toward practical applications of gases, a discussion of some recent findings on polyatomic gases might be appropriate. Thus, a number of electronegative gases, which are particularly of current interest, will be included under this category.

2.2.1 Uniform Field Breakdown

It is apparent from the above review that the Townsend's first coefficient α has the primary importance on gas breakdown and it represents, in essence, the number of ion pairs created by a free electron in collision with neighboring molecules per unit distance of its flight. It is logical that its numerical value should depend on the molecular structure of the gas in addition to the number of molecules per unit volume, or gas pressure, and the electric field intensity. To characterize the gas molecule with respect to ionization by collision, the term cross-section has been used illustratively to give a measure of the collisions between electrons and their neighboring molecules. Devins and Crowe^{21, 22} found that the cross-section Q of a series of saturated hydrocarbon gases can be determined by breakdown measurements according to the expression relating the sparking potential V_s to the gas pressure P and electrode separation d (Paschen's law) as,

$$V_s = KQ(Pd) / \log(CV_s)$$

where K and C are constants for a given gas.

It was found that the cross-section for such a series of gases is proportional to the number of carbon-hydrogen bonds per molecule but is independent of the branching of the molecules. In other words, the breakdown strength of a series of alkanes increases with the chain length and is the same for the branched isomers or corresponding ring structures. This, however, does not readily apply to the unsaturated compounds^{23, 24} such as $(CH_2 = CH_2)$ ethylene, $(CH \equiv CH)$ acetylene, and $(CH_2 = CH-CH = CH_2)$ butadiene. It was pointed out that while the electric strength of a series of unsaturated hydrocarbons (e.g. ethylene, propylene and butene-1), all with double bonds increases uniformly with increasing chain length, that of the other unsaturated hydrocarbons with triple or two double bonds (e.g. acetylene and butadiene respectively) will fall out of line, as seen in Fig. 1. The ordinate can be considered either as the relative electric strength or cross-section of the gas. It is noticed that the double bond series has a higher strength than the saturated hydrocarbon series which was used by Devins and Crowe, and the two double-bond butadiene produces an even greater strength.

The relation between breakdown strength and molecular structure for electronegative gases is different from the hydrocarbon gases because of the electron attachment properties of electronegative gases. As the electrons are attached to gas molecules forming negative ions, they lose their energies and cause no further ionization. Analogously to the Townsend first coefficient α , an attachment coefficient η can be defined as the mean number of attachments per unit length of electron travel in the direction of the electric field. Geballe and Reeves²⁵ have shown that the criterion for breakdown in an electronegative gas is given by

$$[\alpha\gamma/(\alpha-\eta)][e^{(\alpha-\eta)d} - 1] = 1$$

They further pointed out that for a given gas pressure there exists a limiting value of electric field intensity, E , below which η is greater than α and therefore breakdown cannot occur. Under such circumstances electrons are removed faster than they are produced by collision ionization. Crowe and Devins²⁶ have confirmed this experimentally for CCl_2F_2 and SF_6 by breakdown measurement as shown in Fig. 2. The experimental results agreed closely with the limiting values as calculated with the attachment coefficients given by Harrison and Geballe.²⁷

Because of the electron attachment properties, the relation between the electric strength of electronegative gases and their molecular structure is much more complicated. An interesting illustration of the electric strength of a number of such gases relative to those of hydrocarbon gases was given by Works and Lindsay²⁸, as shown in Fig. 3.

They pointed out that the electronegativity per se is not the predominant factor, and the less stable compounds such as CH_2F_2 will have low strength. For some compounds of a given molecular structure, the chlorocarbons are stronger, while for others the reverse is true. It appears that a thorough knowledge of their electron attachment coefficient and of the elastic and inelastic cross-section is required for a more definite correlation of the electric strength of electronegative gases.

The numbers in the circles in Fig. 3 indicate the relative electric strength of a number of gases which may be of practical use as gaseous insulation. Similar comparative values have been given by others²⁶ using the strength of nitrogen as a base for comparison, as shown in Table III.

2.2.2 Non-uniform Field Breakdown

It is recognized by all that although the highest manifestation of electric strength of gases is in a uniform electric field, yet it is often-times not feasible to design electric apparatus without regions of non-uniform fields. Consequently, the strength of gases in non-uniform fields is of considerable practical interest.

The breakdown of air and other simple gases in a non-uniform field such as produced by a pair of rods or spheres is always at a lower voltage than that in a uniform field. A large number of breakdown voltage characteristics for various degrees of non-uniformity is given in a recent book²⁹ which also includes many references for further details. Although the breakdown characteristics are different for different gases or different electrode configurations, yet there is certain regularity in pattern which can be summarized as follows. For moderate non-uniform field electrodes such as coaxial cylinders or sphere gaps, the breakdown voltages increase nearly linearly with increasing spacing as in a uniform field. However, as the spacing between electrodes becomes comparable to and greater than the diameter of either electrode, then the breakdown value increases slowly with increasing spacing. Finally, as the spacing becomes very large in comparison with the dimension of the electrode, local breakdown near the smaller electrode, or that producing higher surface gradient, is practically independent of spacing. This characteristic is illustrated by curves A and B, Fig. 4. In fact, the breakdown voltage characteristics of sphere gaps in the low spacing region are so regular that they have been used for many years as standards for calibrating potentials produced by d.c., a.c., or impulse generators. For high accuracy calibration, however, corrections for air density and the effect of nearby objects³⁰ must be considered. These recent findings are extremely interesting and important in that they show the major influences on the sparkover voltage of the sphere gap to be the proximity of the horizontal ground plane, vertical ground plane and large high voltage conducting parts such as an impulse generator. For instance, with a sphere spacing of one diameter, a change in the distance to the horizontal ground from 5 to 10 diameters increases the sparkover voltage by from 7 to 10 percent depending upon the distance to the impulse generator. Also, if the distance to the impulse generator is reduced from 14 to 4.5 diameters, the sparkover voltage increases by from 2 to 5.5 percent depending upon the distance to the horizontal ground plane.

For very non-uniform field electrodes such as rod or point electrodes, the breakdown characteristics are not so regular. For instance, for a point-to-sphere or a point-to-plane gap, the breakdown voltage increases rapidly with increasing spacing in one region, less rapidly in another region, and becomes unstable in a third region. This is illustrated by curve C of Fig. 4. The shaded area indicates the unstable region.

The irregular breakdown characteristics of very non-uniform fields have been attributed to space charge produced by local ionization prior to breakdown of the gap. For some gases, such as nitrogen, only positive ion space charges can be produced. For air, negative ion space charges due to oxygen are also present which even in a relatively small quantity tend to complicate the breakdown characteristics of an air gap. Finally, for electronegative gases, which can produce a large amount of negative ion space charges upon ionization, the breakdown characteristics have been found to be very irregular.

For instance, the breakdown characteristics of a point-to-plane gap³¹ are schematically shown in Fig. 5. In region 1 it is shown that the breakdown voltages are several times the corona starting voltages. This phenomenon is often termed as "corona stabilization of breakdown". This also accounts for the fact that for a negative point the corona starts at a lower voltage than for a positive point but its breakdown voltage is higher. Qualitatively, one can visualize that corona produces space charge which acts like a shield around the sharp point of the electrode resulting in a less non-uniform field. Because of the negative ion forming ability, the space charges are denser for electronegative gases and so produce a more effective shield. Thus, for a given spacing and pressure, if corona starts at a lower voltage, as it does on the negative electrode, more shielding is produced and a higher breakdown voltage will result.

In region 2, the corona characteristics continue similarly for both positive and negative points. However, the breakdown characteristics are drastically different. For the negative point, the curve continues on with increasing pressure, but for the positive point a sudden large reduction occurs at a critical pressure. Such a phenomenon does not exist for gases that do not form negative ions.

This anomalous phenomenon has been studied by several investigators. Howell³² observed curved spark paths, which were much longer than the gap spacing, apparently propagating along a path away from the region of the space charge. There were similar observations of point breakdowns where a spark actually initiates at the shank instead of at the point of the electrode. As the gas pressure was increased the ionization region was more restricted and the diffusion of the space charge was also reduced. Then the spark paths became straighter and shorter. Consequently, the voltage that was required to cause breakdown became lower because of the shorter path.

Foord³³ stated two necessary conditions for the existence of the phenomenon: (1) that a divergent field configuration with the high field region at the anode be used, and (2) that sparkover occur in a gas which forms negative ions. He postulated that the lateral spreading of electrons at the tip of a Townsend avalanche probably decreases with increasing pressure. This facilitates the production of photons by electron-positive ion recombination. Increase of pressure also increases the absorption coefficients of these photons. Thus the chance of concentrating the energy as a streamer formation across the gap is greatly enhanced.

The subject of space charge was further studied by Works and Dakin³⁴ who used several types of voltage sources (a.c., d.c., and impulse), with both polarities. It was shown that the variation of the a.c. breakdown voltages with increasing pressure followed closely with the positive d.c. sparkover results. Consequently, it appeared that the positive half cycle of an a.c. voltage is more effective in initiating breakdown. It also followed that the space charge produced during the negative half cycle has a negligible effect on the stabilization phenomenon. An interesting result was obtained by comparing the breakdown voltages of a suddenly applied sixty cycle voltage and of a $1.4 \times 40 \mu\text{sec.}$ impulse wave. Since

the impulse breakdown voltage was lower, it appeared that the time required for the space charge to build up was much less than one cycle of a.c. voltage but greater than several microseconds.

The existence of space charge has never been more vividly demonstrated than in the experimental results shown by Berg and Works³⁵. By imposition of two types of voltages, positive d.c. and positive impulse, they were able to show the start of the "corona-stabilization of breakdown" as well as the effect of space charge quantitatively. Fig. 6 shows the total voltage applied (direct plus impulse) as a function of direct voltage applied for SF₆ at two atmospheres. The total breakdown voltage for SF₆ remains constant up to the corona inception voltage. At the corona inception voltage, at which space charges begin to build up, the total breakdown voltage rises with the applied direct voltage bias. The greater the bias above the corona starting voltage, the greater is the total voltage required for breakdown, as shown by the rising portion of this curve.

2.3 Forces and Energies

Mechanical forces developing in a dielectric have recently been discussed by Lee³⁶ carrying on from an earlier paper by Smith-White.³⁷ Similarly, in the discussion by Lichtenstein³⁸ following that of Lee, the thermodynamic approach is extended from that of Abraham-Becker³⁹, by introducing new postulates that the free energy of the system may be localized, and that the stress tensor depends only on the molar volume, the vector electrical displacement and the temperature. The force density concept was evaluated by Lee employing theories of Faraday-Maxwell, Helmholtz, and of Larmor and Livens, in most cases obtaining different results from each. It should be understood that these authors (excepting Abraham, p. 98) are dealing with the liquid or solid state and that the question of the mechanical forces in a gas dielectric is only part of a more general problem. Granowski⁴⁰ deals most systematically with the gaseous state as an "energy reservoir" and incorporates an "inertia factor" as a necessary concept in an electrodynamic gas system. Both kinetic and potential energies are present in the gas. The electrical energy on the electrodes is the sum of the electrostatic and electromagnetic energies represented by:

$$W_E = \frac{1}{2} CV^2 = \frac{1}{8\pi} \iiint \epsilon E^2 d\ell^3 \quad \& \quad W_H = \frac{1}{2} LJ^2 = \frac{1}{8\pi} \iiint \mu H^2 d\ell^3$$

in which ℓ^3 is volume, and the other symbols have their usual significance. Difficulties arise in a convincing presentation of how and why this energy exerts a force on a given volume of neutral molecules. It would seem that the necessary conditions for establishing a dynamic state are conductivity and reactance and these we know are present in the ubiquitous free electrons, no matter how few, and the polarizability of matter, no matter how small. Granowski's contribution resides in the able discussion of the reactive effects in the gas to the magnetic and

electric fields. Among these are the ionization energy, the kinetic energy of charged particles, activation and radiation energies, and non-electromagnetic energy forms. These last rightly include atomic and molecular vibrations and the number of degrees of freedom possible in the particle. The degrees of freedom become significant in polyatomic gases such as the presently important high-strength fluorocarbons and sulfur hexafluoride, as will be shown later.

That the foregoing does not exhaust the possible energy sinks or reservoirs is apparent from other publications. For instance, Camilli and Plump⁴¹ indicated briefly that the electronic configuration of SF_6 is possibly resonant and contributing to the stability of the molecule. Fröhlich and Platzman⁴² have considered the energy loss of moving electrons to dipolar relaxation and Biondi⁴³ has presented a mechanism of diffusion cooling of electrons in ionized gases. Contrary to Morse⁴⁴ who concluded that there was an inappreciable effect on molecular rotation and vibration by electron impact, Gerjuoy and Stein⁴⁵ found a significant effect by slow electrons on the rotational energy alone. The compressibility and dielectric polarization from the statistical mechanical viewpoint, and their relation to the dielectric constant of a polar gas were ably discussed by Buckingham and Pople⁴⁶. More recently, Buckingham⁴⁷ has further developed a theory of dielectric polarization of polar substances, and the electromagnetic properties of compressed gases have been examined by him and Pople⁴⁸.

In all of these, and probably in many others, a healthy preoccupation exists with the forces between molecules, atoms, and electrons. However, among our present high strength dielectric gases an energy sink is common to all which is worthy of note and has already been mentioned. Electron attachment, which Thomson postulated in theory, and Wellisch apparently demonstrated clearly for the first time, both in 1915, has been spasmodically investigated through the years⁴⁹, and now, with the aid of negative ion mass spectrometry, it is being extensively incorporated in our body of knowledge. The importance of taking the attachment process into account when dealing with high strength gases has rather recently been explored by Geballe⁵⁰ and co-workers, as we have seen, although the first recognition of its application in the Townsend theory is probably due to Penning⁵⁰. Hickam and Fox⁵¹, confirming and furthering the experimental work of Ahearn and Hannay⁵², found a very large cross-section indeed for SF_6 which effectively consumes slow electrons. Because there are probably a large absolute number of slow electrons in an impressed field between conductors, converting these to much slower negative ions undoubtedly contributes much to the electrical characteristics of the gas. We are now going through a de-emphasis of the classical ionization potential, and in contrast are viewing, with much concern, the exactly opposite process which involves the energy of combining an electron with a neutral particle to produce a negative ion. Those gases which do not form negative ions are not of high strength and a high classical ionization potential, as is the case of helium, can no longer be considered alone a necessary condition for high dielectric strength.

It is proposed that molecular composition, structure, and forces comprise sufficient grounds for a materialistic approach to the various phenomena of insulating gases. In monatomic gases there is neither molecular structure nor intramolecular forces, only the atomic characteristics of a single nucleus and its cloud of electrons. This is a notoriously weak system. The van der Waal's cohesive force "a" by itself does not contribute much. But in polyatomic gases there are not only the attractive forces between molecules but also interatomic bond energies and forces, as already mentioned. Similarly, among all the electrons in a molecule definite cohesion to the total system is certainly strong or else ionization would be possible at lower field strengths.

As an example of "theoretical empiricism" the results of the following calculations are offered on the postulate that the dielectric strength of a gas is proportional to the cubic root of the product of van der Waal's "a", the summation of the stretching force constants between all the atoms, and the gas pressure divided by the mean free path between molecules. The last column of the following tabulation shows this quantity for four gases at 1 atmosphere (101×10^4 dynes/cm²)

Gas	"a" cm dynes cm ²	Force, "f" constant (dynes/cm)	"L"* Mean free path, (cm)	$\left(\frac{"a" \cdot \sum "f" \cdot 101 \times 10^4}{"L"} \right)^{1/3}$
H ₂	24×10^{10}	5.76×10^5	11.8×10^{-6}	2.2×10^9 dynes
N ₂	1.4×10^{12}	22.5×10^5	6.3×10^{-6}	9×10^9 dynes
SF ₆	4.5×10^{12}	5.1×10	4.9×10^{-6}	14×10^9 dynes
C ₄ F ₁₀	8.6×10^{12}	6.25 (C-F)	3.7×10^{-6}	18×10^9 dynes
		4.5 (C-C)		

These values are in the same approximate order as the relative breakdown voltages of the gases. Dimensionally this column is force, m.l.t⁻², and would have to be multiplied by a distance, L, to conform to the dimensions of energy, m.l.t⁻².

* "L" - by various formulas, see Reference No. 111 p. 857.

3. Practical Developments

Gaseous, liquid and solid insulation are seldom used singly to insulate an electrical device. Even though a piece of equipment is referred to as "gas or liquid-filled" apparatus, solid insulating materials must be used for mechanical rigidity. Thus, it can be said that a gas insulated apparatus is one in which the gas is used as a major insulation or coolant, either in quantity or in the region of high electrical stress. In most power apparatus both insulating and cooling properties of the gaseous medium are important.

The atmospheric air is the most common and plentiful mixture of gases. It has been widely utilized for a long time as electrical insulation. Unfortunately, it cannot be used universally for all electrical apparatus because of certain operating requirements. For instance, if superior cooling properties are sought, hydrogen or helium might be used instead of air. If higher dielectric strength is sought, some kind of fluorocarbon might be selected. The use and evaluation of such gases will be considered here as progress of gaseous dielectrics.

3.1 Rotating Machinery

Early in the 1920's, hydrogen^{53,54,55,56} was studied as a cooling medium for large electrical machinery such as turbine-driven alternators. The important characteristics of hydrogen when compared with air as a cooling and insulating medium for large high-speed electrical machines are manifold. Because of its lower density the windage loss is reduced. Because of its higher thermal conductivity, the heat transfer is increased. In fact, the resultant advantage is the accumulative effect of these factors, because the reduction of windage loss results in less heat to be removed which in turn results in a cooler gas when it returns to the machine.

Although hydrogen is the best gas for cooling, it also represents the most difficult problem in shaft-sealing especially for large size, high-speed turbo-generators. A definite step toward the utilization of hydrogen-cooling was realized by the simplified shaft seal oil system⁵⁷, about 20 years after the introduction of hydrogen cooling. Experience with such a system proved that much of the conventional auxiliary equipment, such as continuous recording of hydrogen conditions, vacuum treatment of the oil, drying of hydrogen, etc., is not necessary. Thus, operation of hydrogen-cooled turbo-generators became fully automatic⁵⁸ with alarms for low hydrogen pressure, low "seal-oil" pressure and pressure of liquid in the gas. The maintenance duties became only slightly more than for an air-cooled machine.

The quantitative advantage resulting from the use of hydrogen naturally depends on the design of the machine. However, it is predictable that higher efficiencies can be obtained when the hydrogen pressure is increased to several atmospheres. Such a scheme has been realized in more recent years.^{59,60}

The effect of increasing hydrogen pressure is to increase the density of the gas and thus its capacity to absorb heat. However, the overall heat transfer by the gas is not linearly proportional to the increasing pressure because the thermal drop through winding insulation and iron core are independent of pressure. It has been a usual practice to allow one percent increase in the output capacity for a one psig increase in pressure for the range up to 15 psig and two-thirds percent psig from 15 to 30 psig. Higher efficiencies and output capacities can be obtained by the supercharged hydrogen cooling systems^{59,60} in addition to the pressurized hydrogen.

There are, however, certain disadvantages of increasing gas pressure for cooling of rotating machinery. For instance, the pressure developed by the blowers, the back pressure of the ventilation circuits and the windage loss all increase directly with pressure, although some of the drawbacks only cause a slight reduction of the overall efficiency. Since continuous increase of gas pressure over 15 to 30 psig will reach diminishing returns, inner cooling of the windings through the inside of hollow conductors, using either gas^{61,62} or liquid⁶³, has been developed. In this case the gas pressure has been increased to 45 to 60 psig, while experimental data have been obtained at pressures as high as 90 psig. Preferred standards⁶⁴ for large hydrogen-cooled turbine generators have been proposed for a hydrogen pressure of two atmospheres.

3.2 Transformers

While hydrogen gas was used in rotating machinery mainly for effective heat transfer and low windage loss, another group of gases with much higher dielectric strength was investigated for static electrical apparatus such as x-ray and power transformers. These gases can be, in general, classified as electronegative gases containing one or more electronegative elements such as fluorine or chlorine in their molecular composition. Typical examples are the series of Freons:

F-12 (CF_2Cl_2), F-22 (CHClF_2) etc., fluorocarbons: C_3F_8 , C_4F_{10} etc., and various forms of fluorides: SF_6 , SeF_6 , etc. By virtue of their ability to form negative ions in an electric field, which gives rise to high dielectric strength^{65,66}, they are primarily used for their insulating properties. Moreover, because these gases have in general higher molecular weight than air, their heat transfer characteristics are also superior.

As in the case of rotating machinery, the use of elevated pressure of these electronegative gases is advantageous in application. The success of using high pressure SF_6 for very high voltage X-ray transformers or generators has been demonstrated⁶⁷. With the improved techniques of constructing pressure containers and of leak detection, SF_6 has at over a hundred pounds per square inch pressure has been utilized to insulate such transformers operating at several million volts.

Although high pressure SF_6 gas has been successfully used for x-ray transformers for over two decades, similar applications for transformers in power and electronic fields have not been capitalized on until more recently. This delayed action is essentially due to the differences in operating requirements. The three major ones are the differences in ambient temperature, electric field and power dissipation.

The variation of ambient temperatures for x-ray transformers, as they are used indoors, is relatively small, whereas that for power transformers in the field or for very special electronic applications encompasses a large range. If the ambient temperature falls below the liquefaction point of the high pressure gas, condensation will occur in the transformer before it is put in operation. This not only causes a reduction in the gas pressure but also may produce droplets on metallic surfaces. Both would impair the dielectric strength of the insulating structure and therefore must be considered in design and in the advanced evaluation of such an occurrence. On the other hand, if the ambient temperature is too high so that the efficiency of heat transfer is greatly reduced, then the gas temperature may increase over the limit at which decomposition of the gas may occur in the presence of other materials used in the transformer. Such is not the problem for ordinary applications or for x-ray transformers where the heat to be dissipated to the ambient is relatively small.

Secondly, due to the design requirements, the electric fields in x-ray transformers are essentially uniform between the high and the ground potentials. In such electric fields the dielectric strength of the electronegative gases increased almost linearly with increasing pressure. However, in power and other transformers where it is not economically or technically feasible to avoid non-uniform electric fields, an unduly undesirable reduction^{68,69,70} of the gaseous dielectric strength may result.

Thirdly, the power dissipation of an x-ray transformer for intermittent operation is an irrelevant factor in its design or operating considerations. However, an inefficient heat transfer from the core and coil of a power transformer may result in hot spots where slight gas decomposition or weakening of the coil insulation may occur. To avoid such damage, forced circulation of gas⁷¹ or vaporization cooling techniques⁷² for power transformers, or liquid evaporation process through the use of wicks for electronic transformers, have been introduced.

Although advances have been made to increase the practicability of using gaseous insulation for power transformers to replace liquids, it will be a number of years before the transition can be made. However, due to the fundamental superior properties of gaseous insulation such as higher thermal stability, higher dielectric strength with pressure, and non-inflammability, it is only a matter of time when more transformers will be built with gaseous insulation.

3.3 Cables, Waveguides, and Current Interrupting Devices

Oil-filled cables have been successfully used for a long time. However, small voids in the oil-impregnated insulation have limited its ultimate electric strength. This prompted the more recent development of high pressure gas-filled cables. The thought behind this development was that the pressurized voids, if any, would have a higher ionization level than voids of lower pressure. This principle of void control, in addition to the advent of the seamless aluminum sheath, has brought about the successful operation of gas-filled cables^{73,74,75,76}.

The application of gaseous insulation in cables is different from that in transformers. Because of the concentric geometry, the gas pressure with nitrogen for instance, may run as high as several hundred pounds per square inch without much concern for mechanical bracing. However, because of the long length and multiple joints, gas leakage becomes a more serious problem. Consequently, leak detection methods have been developed for cables⁷⁷ as well as for transformers.⁷⁸

Power factor and stability are important considerations in cable operation. It was found that the power factor of gas-filled cable can be maintained at a relatively low value under adverse cycling conditions. Since the power factor of gases without ionization is inherently lower than liquids, it is conceivable that gas-filled cable should in time replace liquid impregnated cables where dielectric loss is the major criterion.

It may be remarked here that when a cable is connected to a transformer, such as in an underground system, a d.c. test of the cable is undesirable if the transformer is liquid-filled. The d.c. strength of a liquid-filled transformer may be lower than its a.c. strength, because the higher conductivity of the liquids in comparison with the solid insulation used in series with them, produces higher stress in the solid insulation than that in the case of a.c. test. This condition is largely eliminated for gas-filled transformers because the conductivity of gases is low under both a.c. and d.c. voltages.

Sulfur hexafluoride gas has been used not only in transformers and telephone cables, but is also being evaluated for use in waveguides^{79,80}. Since waveguides are used to transmit radio frequency energy, the evaluation was made in terms of power rather than dielectric strength. At radar frequencies the power breakdown was seven to eight times that of air under similar conditions.

In these and other investigations, a phenomenon often encountered is the decomposition of the gas under arcing conditions or even below visual ionization. Strictly speaking, decomposition was observed over a long period of time under the latter conditions⁸¹. Certainly, a variety of decomposition products are found under electrical discharges⁸². However, in some practical applications where decomposition is not necessarily intolerable (or the limiting factor), gas insulation can be used even under intermittent arcing conditions.

It is a common experience that when a gas-insulated structure is tested to failure without a powerful arc, the dielectric strength of the structure is not greatly reduced. If the failure path lies totally in the gas, the failure can be remedied by removing the ionized gas quickly from the highly stressed region. Of course, the high voltage air circuit breakers are operated under this principle. These breakers are invading the market, as well as matching the performance, of oil circuit breakers.

More recently the arc-quenching property of gases is being investigated and circuit breakers are built with sulfur hexafluoride⁸³ for its excellent arc quenching behavior. The gas pressure used in this 115 KV, 3-phase circuit breaker was 45 psig in comparison with several hundred pounds of pressure commonly used in compressed air circuit breakers⁸⁴. The interruption time ranging between 2.5 and 3.5 cycles of power frequency is comparable to that of the high quality oil-circuit breakers. The restrike-free performance of interrupting fault and magnetizing currents, and switching capacitive currents are noteworthy.

Experimentally^{85,86} it was found that the a.c. interrupting ability of plainbreak arcs in SF_6 is in the order of one hundred times that of similar arcs in air. At 2,300 volts, the limiting arc current in amperes is approximately equal to, in numerical values, fifty-five times the absolute gas pressure in atmospheres. It is interesting that such a linear relationship is similar to the gain in dielectric strength with increasing pressure in a uniform electric field. Also, in this experiment the effect of arc-producing decomposition products was considered. Their experiences have shown that with SF_6 the effect is less serious than anticipated. The decomposition products⁶ were formed at only a moderate rate and may be absorbed readily by such materials as activated alumina. This was later substantiated by the 115 KV circuit breaker life test of over 1,500 unit operations under conditions more severe than that specified by standards.

These findings also prompted the evolution of a new load interrupter switch⁸⁷. The use of SF_6 gas here has resulted in reducing the contact separation to only 6.5 inches for 115 KV units, and 3.5 inches for 34.5 KV circuits. Such a switch is not only small and lightweight, but also requires no external supply of gas or other auxiliary apparatus for operation.

Considerable gains in the use of SF_6 in condensers and capacitors were recorded in Russia during the 1940's. Possibly the reason for a lack of information on present day applications is due to a disinterest on the part of manufacturers. No significant gain in capacity can be expected in changing from one gas to another. However, Hoxhberg et al^{88,89} found for heavy loads. i.e., 2,000 kv-amp. at 1200 μmf capacity, that SF_6 at 8-9 kg./sq.cm. would be preferred over N_2 at 15-18 kg./sq. cm. The range of condensers tested was from 300-4,000 uuf, with a peak voltage of 40 KV at 1.2×10^6 cycles/sec.

3.4 The Patent Literature

Applications from the practical standpoint are exemplified in the patent literature. For instance, one of the earliest patents recognizing the value of nitrogen, and nitrogen helium mixtures in a pressurized transformer was issued to F. S. Smith⁹⁰ in 1933. Seven years later F. S. Cooper⁹¹ claiming the use of CCl_2F_2 and of SF_6 , and P. D. Ritchie⁹² who recognized the advantages of the aliphatic perfluorocarbons (e.g. C_3F_8) were the first to capitalize on present high strength gases. In 1943 H. Skilling⁹³ obtained his patent and then nothing more appeared until 1951 when C. F. Hill⁹⁴ obtained his patent on the use of perfluorocarbons or chlorofluorocarbons boiling above 50°C and up to 225°C for the vaporization cooling of nitrogen-filled transformers. Meanwhile, L. J. Berberich and C. N. Works⁹⁵ had been extending their investigations on a broader scope for high molecular weight fluorocarbons, ethers, and amines as dielectric strength elevators in nitrogen. Recently, T. E. Browne, Jr.⁹⁶ et al, claiming selenium hexafluoride, and H. J. Lingal⁹⁷ claiming SF_6 , both in circuit interrupting devices having fast arc-quenching ability, were granted patents. In all cases the disclosures are highly informative. For example, increasing quantities of perfluoromethylcyclohexane added to 74 cm. of nitrogen raised the breakdown strength as much as five times that of the nitrogen. The smaller additions produced the most dramatic results, being out of proportion with simple linear composition.

4. Chemical Properties and Effects

For practical applications it is obvious that a knowledge of the chemical and physical properties of a gas is essential. For example, the generally favorable characteristics of sulfur hexafluoride have been known for some time and attention was directed to this gas in 1951 by Camilli, Gordon and Plump⁹⁸, and earlier by Hoxhberg⁹⁹. The properties of some of the Freons and fluorocarbons were reviewed later.

4.1 Thermal and Chemical Stability

Next to dielectric strength, the property of inertness is perhaps of major importance. The material which contains the gas, and the internal parts of an electrical apparatus may have an appreciable effect on the "life" of the gas, as has already been mentioned. In the laboratory where glassware rules, a gas may be quickly appraised and too soon labeled as a stable compound. Contact with metals at much lower temperatures than in glass may tell a very different story. This is well known today.

Borosilicate glass as a container material, however, has proven to be satisfactory in the authors' laboratory in the form of sealed capsules of 20 mm. inside diameter and about 25 cm. length, having a short length of 8 mm. tubing at one end for final sampling. The technique of introducing a test piece of constructional material, evacuating, flushing, filling with gas (a little above one atmosphere) freezing out, and sealing, is conventional. In the temperature range of 150°C to 300°C, and higher, these life test tubes have shown deterioration of test samples, after long exposure times, of a number of different fluorogases before any apparent attack of the glass had set in, unless gas deterioration on the test piece was so extensive that the products then were capable of attacking the glass, in which case a white opacity was an additional obvious sign of chemical breakdown, and a marked difference in stability between 200°C and 300°C may be found. Fig. 7 illustrates this effect.

This tube method of testing can be adapted to higher pressures of gas and, in this case, shorter times and a more drastic evaluation are procured due to the mass action principle. Publications by Kvalnes et al.¹⁰⁰ are very helpful in this respect.

A high stability of sulfur hexafluoride and some fluorocarbons (though naturally not equal to that of nitrogen), has been confirmed by the above method of testing on silicon steel, copper, and especially aluminum. A well-cured silicone varnish on these metals has adhered for over a year at 200°C in SF₆ and shows only slight darkening. At 150°C after more than three years, aside from bare metals becoming dull, various fluorogas systems appear to have an indefinitely long life. However, it appears that much practical work will have to be done by people in industry employing their specific materials under certain conditions. The available literature^{101,102,103} is of great interest in demonstrating the usefully inert character of most fluorogases, but there is just not enough of it.

4.2 Flammability

Chemical inactivity is more particularly illustrated by nonflammability and this property is universal among the fluorocarbons, chlorofluorocarbons, and sulfur hexafluoride. In all cases, starting from the free elements, the free energy change in going to the compounds is so large that the chemical potential for further reaction with oxidizing agents is very small indeed.

4.3 Toxicity

There is, furthermore, an oversimplifying temptation to regard substances of very low chemical reactivity as also being non-toxic. It is true that adequate physiological testing in vivo¹⁰⁴ has established a high probability of human safety in massive exposures to purified sulfur hexafluoride, many chlorofluorocarbons, and some fluorocarbons, and even when samples of these are known to be noxious as, for example, after being decomposed in an electric arc, there is still a margin of no great danger. A chemist knows from personal experience that at some time through exposure to materials of his profession, he should no longer be here, were it not for the survival power of human physiology. This knowledge however does not advise, nor should engender, a foolhardy attitude toward a substance which is inevitably deadly in a critical combination of exposure time and concentration. Dr. Lester¹⁰⁵ has reviewed, summarized and explained the phenomena of toxic effects for the benefit of electrical engineering, by dealing with laboratory results on dielectric gases as well as presenting considerations of a broadly illustrative nature. For example, a physiological classification of gases should include simple asphyxiants, chemical asphyxiants (such as CO and HCN), irritants, and drug-like compounds. Lester and Greenberg¹⁰⁴ were the first to show that sulfur hexafluoride (also perfluoropropane, unpublished) falls in the first class. These gases, therefore, must reduce the oxygen content of air to about 13 percent by dilution before a seriously lethal asphyxiant action will develop.

Many "Freons" have been commercially investigated¹⁰⁶ for relative toxicity. The results show generally a very favorable position for these substances in the numerical scale used as an index.

In summary, purified dielectric fluorogases are generally innocuous but a check on this point should be made with the manufacturer, especially if a new gas is developed. In any case, a minimum concentration and a maximum exposure time exist for practically all poisons, below which the chances of recovery are excellent. Finally, however, no unnecessary or avoidable risks in the handling of any gas should be tolerated. As Lester has put it, "One may choose whether or not to swallow or come into contact with a solid or liquid; no such alternative is, in many instances, readily available with a gas."

4.4 Ease of Production, Purification, and Re-use

Sulfur hexafluoride has been obtainable for many years because of its direct and relatively simple synthesis from the elements. True, elemental fluorine is not so easy to handle nor is it inexpensive, but given a workable technology and abundant resources, the output is then only limited by the size and number of fluorine generating cells, and the rate at which sulfur can be transported from the mine. The purification of the crude gas mainly depends upon the pyrolytic disproportionation at 200-300°C of S_2F_{10} which may be present, followed by caustic scrubbing to remove the lower valent fluorides of sulfur. Fluorocarbon production and purification are fundamentally not so straightforward; elemental fluorine combining with carbon produces a wide ranging mixture including CF_4 which dielectrically has little, if any, advantage over air or nitrogen. To stop at this point, however, would not be fair; the direct synthesis from hydrocarbons reacting with fluorine or polyvalent metal fluorides such as CoF_3 or AgF_2 can be accomplished. Greater processing control seems to be required, and regeneration of the spent metal fluorides is necessary. This, however, leads us to the one process which is really competitive and practical: the substitution of fluorine for chlorine in chlorinated hydrocarbons. In this case, relatively inexpensive starting materials are converted by antimony trifluoride, oxidized by chlorine to the pentavalent state, in hydrogen fluoride to highly fluorinated compounds, as Swarts discovered and the "Freons" testify. If the hydrocarbon was fully chlorinated to begin with, substituting the last one or two chlorine atoms by the above reagent is extremely difficult, and the more active metal fluorides mentioned earlier, or elemental fluorine must be employed for the final step if a fully fluorinated hydrocarbon is demanded. Nevertheless, technical progress now appears to be at a point where the high prices of a few years ago no longer seem tenable, and the belief now appears justified that the cost of insulating space by fluorinated compounds should fall within the economics of the electrical industry.

For the adequate purification of a selected gas a variety of procedures are available such as fractional distillation or freezing, chemical reagents for chemically active contaminants, and selective absorbents (gas chromatography) about which much has been learned lately. Activated alumina has long been a favorite adsorbent for both purification and drying but others are appearing which may be capable of demonstrating higher efficiencies. It is very likely that each manufacturer has worked out a purification procedure, the sequence and details of which he is rather secretive.

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The user of gas in the electrical industry will find that occasionally an apparatus containing the gas will have to be emptied because of some reason or other, and the dilemma will arise whether to allow the gas to escape or attempt to reclaim it. Of course the controlling factor will be the quantity and value involved. It is fortunate, however, that the dielectric fluorogases can be handled with fairly low compression backed

up with attainable low temperature. By this is meant that a power transformer can be emptied of sulfur hexafluoride if a gas compressor of only a hundred psig is connected to the supply of SF_6 , and a previously evacuated steel gas cylinder, cooled and held at -50°C by surrounding solid carbon dioxide and alcohol, receives it. Fluorocarbons generally condensing at higher temperatures than SF_6 will require less compression and/or cooling. Their relatively low latent heats of evaporation per pound are sparing of the cooling agent and at the same time provide fast condensation.

5. Physical Properties and Effects

5.1 Condensability

This matter of condensation is of serious concern if the equipment containing a rather high boiling point gas must operate out-of-doors in a cold climate and if the electrical strength of the unit depends upon all the gas being in the vaporized state. Obviously a substance with a boiling point of 0°C at one atmosphere of pressure will not all be in the gaseous condition in a container originally filled with the gas at room temperature and a few pounds of excess pressure, if the temperature falls below 0°C . Some of the gas will condense to the liquid state and the gas remaining will be at a pressure equal to the vapor pressure of the liquid, and this in turn will be a characteristic of the substance chosen. Temperature vapor pressure curves and data are available for the presently considered group of dielectric gases, and in general, any gas with a boiling point below that of C_4F_{10} (2.5°C) will have a vapor pressure at -40°C not less than 1.5 psia. It follows that some gases will of course have a much higher vapor pressure than 1.5 psia at -40°C .

This is fortunate because it allows a combination of gases to be used for a high dielectric strength with assurance that the strength will be maintained even when the temperature falls. The mixture can be so chosen according to the principles of physical chemistry concerning partial pressures that a close approximation can be obtained to match a particular set of circumstances. For example, the dew points of various concentrations of perfluorocyclobutane in nitrogen were required in order to predict the temperatures and pressures at which condensation to the liquid phase should take place. A simple apparatus was constructed of a glass vessel (vol. 250 cc) provided with an internal magnetically driven stirrer, connecting tubes to the gas supply, manometer and pump, and a central thin glass well containing a thermometer and methanol into which powdered dry ice could be dropped. The well was internally silvered in case a true fog might be seen on it. When judicious quantities of solid carbon dioxide had cooled the well sufficiently in mixtures of the fluorocarbon and dry air, each measured by its pressure on the manometer, a slow and steady drip would occur without first visibly clouding the glass.

These drops were small because the liquid has a high density and low surface tension. The temperature at which dropping occurred was evidently not an equilibrium temperature, so with the aid of the stirrer, which vaporized the droplets as they fell on it, the cold well was allowed to warm up, generally $0.5 - 3.0^{\circ}\text{C}$, when the dropping stopped and the temperature was read as being most nearly at the dew point.

The success of this rather crude experiment is demonstrated in Fig. 8. The solid line is the known vapor pressure curve for octafluorocyclobutane; the circles are the experimentally obtained dew points of this substance in dry air at the partial pressures given by the manometer. The concentration of the fluorogas ranged from 16.7 percent to 100 percent and the total pressures of the combined fluorogas and air were from 820 mm. to 1020 mm. Hg. The generalized conclusion is that a good approximation of the temperature and partial pressure at which a given gas in a mixture will condense can be obtained from its vapor pressure-temperature curve.

5.2 Heat Transfer

The double service of providing an electrically insulating medium and at the same time an aid to the dissipation of heat will widely be demanded of a gas or mixture of gases. Cobine¹⁰⁷ was aware of this when he investigated combinations of helium and sulfur hexafluoride, in comparison with the gases singly, and with air and hydrogen. The last has been rather extensively studied¹⁰⁸ for heat transfer purposes in generators, as already mentioned, where its low dielectric strength can be mitigated. Helium, with even lower strength, would be second choice based on published and tabulated thermal conductivity coefficients. Hydrogen and helium consequently occupy favored positions in classical heat transfer practice and theory. Yet the "heat transfer" as measured by Cobine, meaning "the power input necessary to maintain a constant temperature of the wire at the center of the helix" was approximately 5 for SF_6 , 3 for H_2 , 2.3 for He, and 1.5 for air, in watt units at 100°C . It followed that any combination of sulfur hexafluoride with helium was superior to air; the important datum appeared in the fact that concentrations of SF_6 greater than about 27 percent in He produced a heat transfer efficiency exceeding that of H_2 . The dielectric strength of a 20 percent SF_6 concentration in He exceeded that of air (and of course those of H_2 and He by large margins) in a 0.1 inch gap between 1 inch hemispheres with sixty-cycle applied voltage. In competition with hydrogen for use in rotating devices, a mixture of sulfur hexafluoride and helium most seriously would suffer from an increase in windage loss. The gains in heat transfer efficiency, nonflammability, and dielectric strength would have to be balanced against this loss. The fact remains that SF_6 has been confirmed as a very effective gas for heat transfer as was indicated in earlier studies of a few years ago.

For practical purposes it is well to distinguish immediately between "heat transfer" and the classical coefficient of thermal conductivity which may be downright misleading unless one takes into account the implication along the route of its theoretical development.

The simplest expression for the coefficient of thermal conductivity, attributed to Maxwell, is given by:

$$k = K \cdot \eta \cdot c_v$$

which has the dimensions of $\text{m.l. t}^{-3} \cdot \text{T}^{-1}$ and which can be interpreted as calories per second per centimeter per degree centigrade if η is in poises and c_v is in calories per gram (the specific heat) at constant volume. The constant K is characteristic of the gas and is presumably independent of temperature and pressure¹⁰⁹.

The following tabulation contains the above parameters for a few gases under consideration. Nothing in this table indicates that SF_6 should be as practically efficient as it turns out to be.

Gas	$k \times 10^5$ at 0°C	$\eta \times 10^4$ at 0°C	c_v calories per gram	K
H_2	36.3	0.852	2.406	1.76
He	32.7	1.883	0.753	2.31
N_2	5.14	1.673	0.175	1.76
SF_6	3.3	1.43	0.137	1.68

In theory, the thermal conductivity should be measured in the absence of convection, as for example between closely spaced horizontal plates. It is noted that in Cobine's apparatus a practical heat transfer effect was obtained by making no attempt to minimize convection. A linear relation between the logarithms of the watts input and the temperatures over the range studied, was found. In the present writers' laboratory employing forced circulation of SF_6 at feasible velocities and temperatures a simple linear relation of heat transfer with either temperature or velocity was found, and nitrogen for comparison was considerably inferior to sulfur hexafluoride.

In practice, therefore, where convection is welcomed as an aid, or when its beneficial action is augmented by a blower, the choice of one gas over another may depend upon an empiricism determined by the particular application, and specific requirements. In a closed system, the heat capacity per mol, not per gram, is the important parameter for judgment. For example, air with a specific heat greater than SF_6 falls far

short on a volume for volume basis because with SF_6 146 grams are effectively working when it is possible to employ only 28.9 grams of air. Put in another way, the molar heat capacity of SF_6 compared with that of air is in the ratio of (146×0.137) to (28.9×0.171) and this illustrates the true compositional difference between the two gases. Incidentally, the molar heat capacity of hydrogen is quite low, being only 2×2.4 at constant volume, practically identical to that of air. Here, of course, the velocity of the molecules, these being the real heat carriers (ignoring black body radiation for the moment) provides the superiority of hydrogen over air, but not, however, in direct proportionality with velocity.

A growing understanding of molecular gas heat transfer, therefore, must deal with an increasing number of factors. Not the least of these is the radiation emissivity of Stefan-Boltzmann, Q_B , which transports heat proportionally to a material constant σ and to the fourth power of the absolute temperature, $Q_B = \sigma T^4$. It follows that the higher the operating temperature, the more heat transfer will occur by radiation and above our presently considered upper limits for electrical apparatus, radiation almost independently of the material will account for practically all cooling effects. This is the same kind of heat that we receive from the sun, traveling through great distances of vacuum. This energy passing through a gas is absorbed by the molecules and if these are polyatomic, i.e. having three or more atoms per molecule, or if the molecule is diatomic and has an electromagnetic dipole, characteristic frequencies in the infrared will be energized. The contribution of the infrared spectra of carbon dioxide, water, and a few other gases to total heat transfer from the engineering standpoint has been reviewed by Hottel¹⁰. More general considerations are in order here.

As early as 1856-7, Clausius¹¹, with unique vision at that time, indicated the necessity of visualizing motions of translation, rotation and vibration in the case of polyatomic molecules. (The vibrational frequencies account for infrared absorption). Later, Boltzmann devised a correlation between the number of degrees of freedom representing these motions, and kinetic theory employing the gas constant R (1.98 calories) to predict C_v , the heat capacity per mol of gas. The contribution to C_v was calculated to be $1/2 R$ per degree of freedom, and the total value of C_v was simply obtained by multiplication of the two quantities. According to harmonic theory, a polyatomic molecule of n atoms has three degrees of freedom per atom in the system and these are additive, making the total degrees of freedom equal to $3n$ and this will include three for translatory motion and two or three for rotation.

SF_6 , therefore, has a total of 21 degrees of freedom and the product of these with $1/2 R$ gives for the molar heat capacity at constant volume a value of 20.8 calories, i.e. 146 gm. of SF_6 confined as a gas in a fixed volume should require 20.8 calories to raise its temperature 1°C .

Dichlorodifluoromethane, CCl_2F_2 , molecular weight 121, containing five atoms/molecule should have a C_v of $5 \times 3 \times 1/2 \times 1.98 = 14.85$ calories. These are certainly in the right order. Consider C_3F_8 ; its C_v should be 32.7 calories, and it will be interesting to see if this is confirmed experimentally.

This last gas is not as multiatomic as some fluorocompound vapors recently studied and reported by Ahearn, Kilham and Ursch^{113,112}. These authors effectively demonstrated an easy control of the temperature of an airborne current regulated d.c. power supply of 1,500-2,800 volts having 1,000 watts to be dissipated. A small built-in fan was used to circulate the gases tested which included SF_6 , $\text{SF}_6 + \text{He}$, $\text{SF}_6 + \text{O}_2$,* and N_2 . The rise in temperature over the case temperature (85°C), was a little more than half when $\text{SF}_6 + \text{O}_2$ at 9 psig was compared with N_2 at 5.5 psig on one of the vital parts of the apparatus. With SF_6 alone at 3 psig the temperature rise was about two-thirds that with N_2 . With even heavier vapors, those of $\text{C}_8\text{F}_{16}\text{O}$, molecular weight 416, boiling point 101°C) partly from experiment and partly from engineering formulae, forced circulation with equal fan horse-power should result, with equal heat input, in a relative temperature rise in the gas of only 24 percent that of air, both at the same pressure. The surface being cooled by the vapors of $\text{C}_8\text{F}_{16}\text{O}$ should increase in temperature only 40 percent that found with air. The product of mass and velocity is a controlling factor, but perhaps superficially.

The foregoing has been dealt with at some length not only because progress is evident, but also because our understanding of heat transfer with modern heavy gases still appears to be incomplete. A unifying simplified procedure and theory seems to be needed in the field of polyatomic gases.

*Minnesota Mining and Manufacturing Co., St. Paul, Minn. U.S.A.
 $\text{C}_8\text{F}_{16}\text{O}$, Molecular Weight 416, Boiling Point 101°C

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Table I

Townsend's First Coefficient α As A Function
Of Electric Field E (V/cm) and Gas Pressure p (mmHg)

E/p	p	α/p
20.0	380.0	0.000034
22.0	380.0	0.000052
24.0	380.0	0.000134
26.0	380.0	0.000234
28.0	380.0	0.000430
30.0	380.0	0.000910
31.0	380.0	0.00136
32.0	380.0	0.00201
33.0	380.0	0.00305
34.0	380.0	0.00459
35.0	380.0	0.00605
36.0	380.0	0.00820
40.0	25.0	0.0167
50.0	9.95	0.0554
60.0	4.90	0.127
70.0	1.000	0.224
80.0	0.980	0.340
90.0	0.970	0.491
100.0	0.960	0.637
110.0	0.975	0.806
120.0	0.975	1.007
130.0	0.973	1.236
140.0	0.950	1.477
150.0	0.990	1.602
160.0	1.000	1.758

Table II

Townsend's Second Coefficient γ As a Function
Of Electric Field E (V/cm) and Gas Pressure p (mmHg)

E/p	p	γ
120	0.975	0.00058
130	0.973	0.00062
140	0.950	0.00040
150	0.990	0.00063
160	1.000	0.00094

Table III

RELATIVE STRENGTHS OF ELECTRONEGATIVE GASES

P(Pressure in mm), δ (Electrode Spacing in cm), V_s (Sparkling Voltage)

FORMULA $V_s/V_s(N_2)(P = 50)$ B.P., °C.			FORMULA $V_s/V_s(N_2)(P = 50)$ B.P., °C.		
CH_2F_2	0.74	---	SF_6	1.84	-63.8
CH_4	0.77	-161.5	CF_2Cl_2	2.06	-29.8
CHF_3	0.82	- 82.5	CH_3I	2.09	42.5
CH_3Cl	0.87	- 24.2	CF_2ClCF_3	2.11	-38.7
CF_4	0.89	-128.0	C_4F_{10}	2.34	+ 2.5
CH_2FCl	1.06	---	$c-C_4F_8$	2.44	- 6.0
CH_3Br	1.16	3.6	CF_2ClBr	2.71	- 4.0
CHF_2Cl	1.17	- 40.8	CF_2ClCF_2Cl	2.97	3.6
CF_3Cl	1.27	81.4	$CHCl_3$	3.01	61.3
CH_2Cl_2	1.31	40.1	C_5F_{12}	3.03	25
C_2F_6	1.46	- 78.3	$CFCI_3$	3.18	23.8
CF_3Br	1.49	- 60.0	C_6F_{14}	3.82	52.0
C_3F_8	1.74	- 37.8	$CFCI_2CF_2Cl$	3.93	47.6
$CHFCI_2$	1.82	8.9			

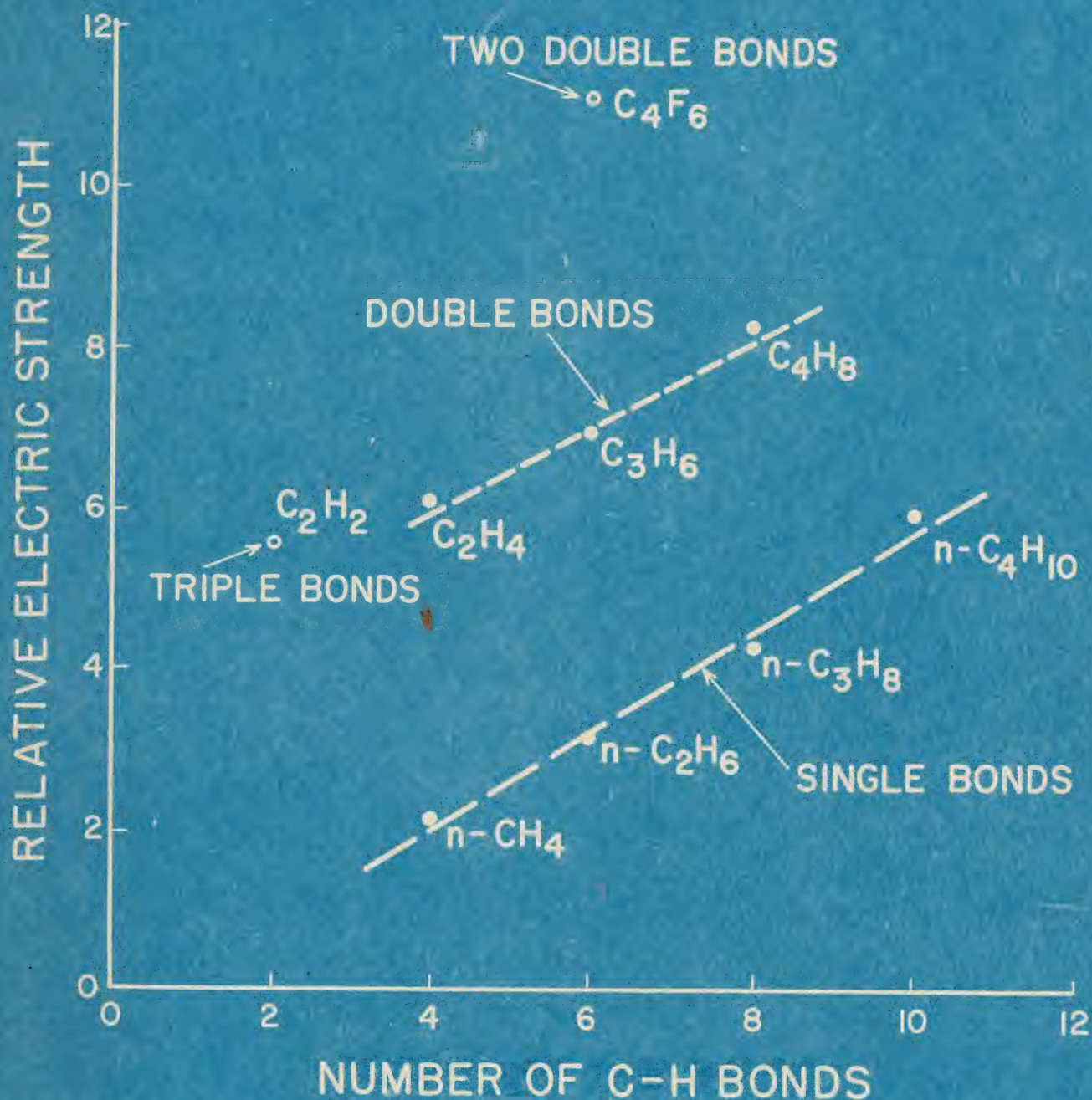


FIG. 1 RELATIVE ELECTRIC STRENGTH
OF HYDROCARBON GASES
(SATURATED AND UNSATURATED)

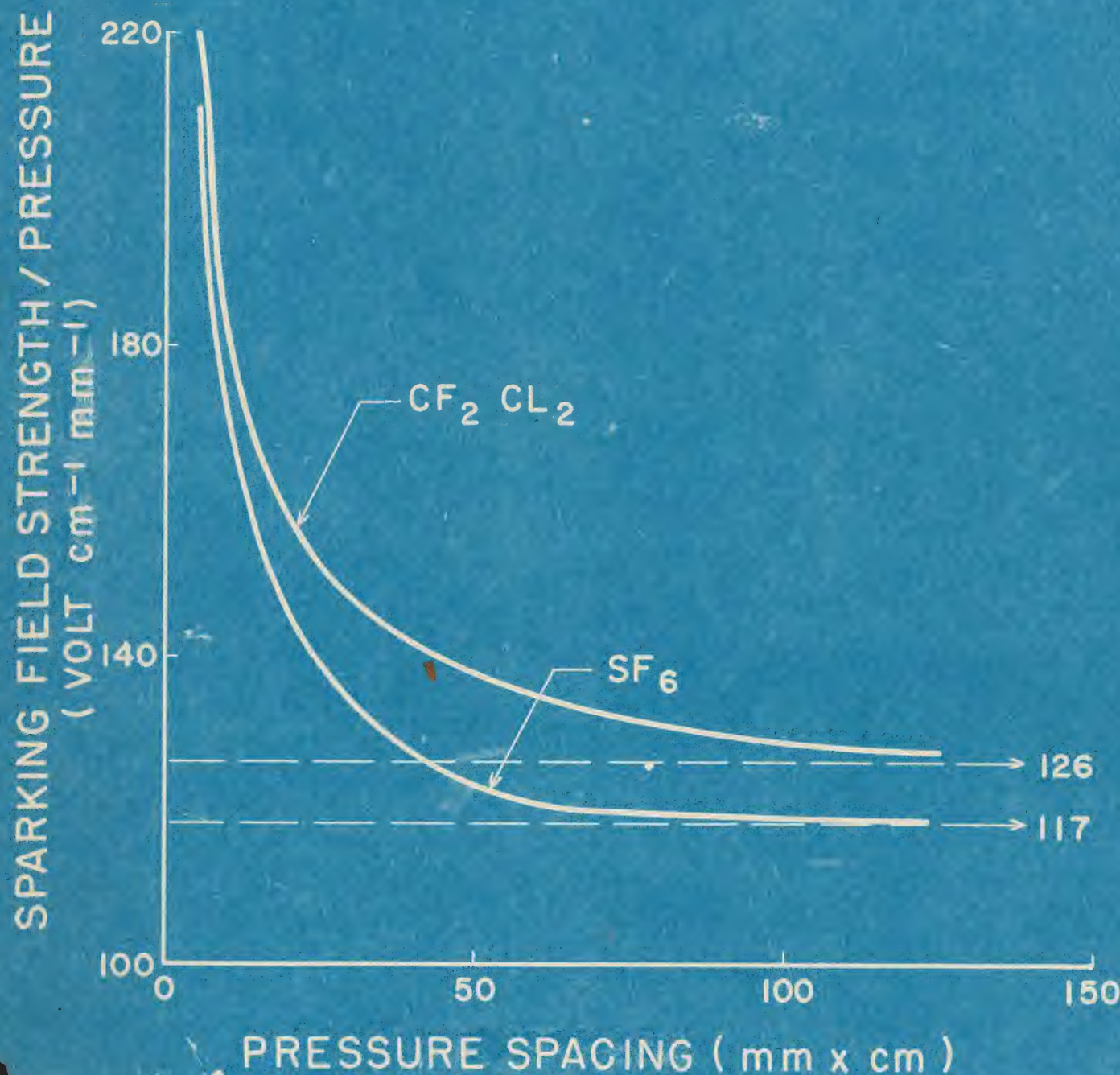


FIG. 2 BREAKDOWN CHARACTERISTICS OF THE ELECTRONEGATIVE GASES IN A UNIFORM FIELD

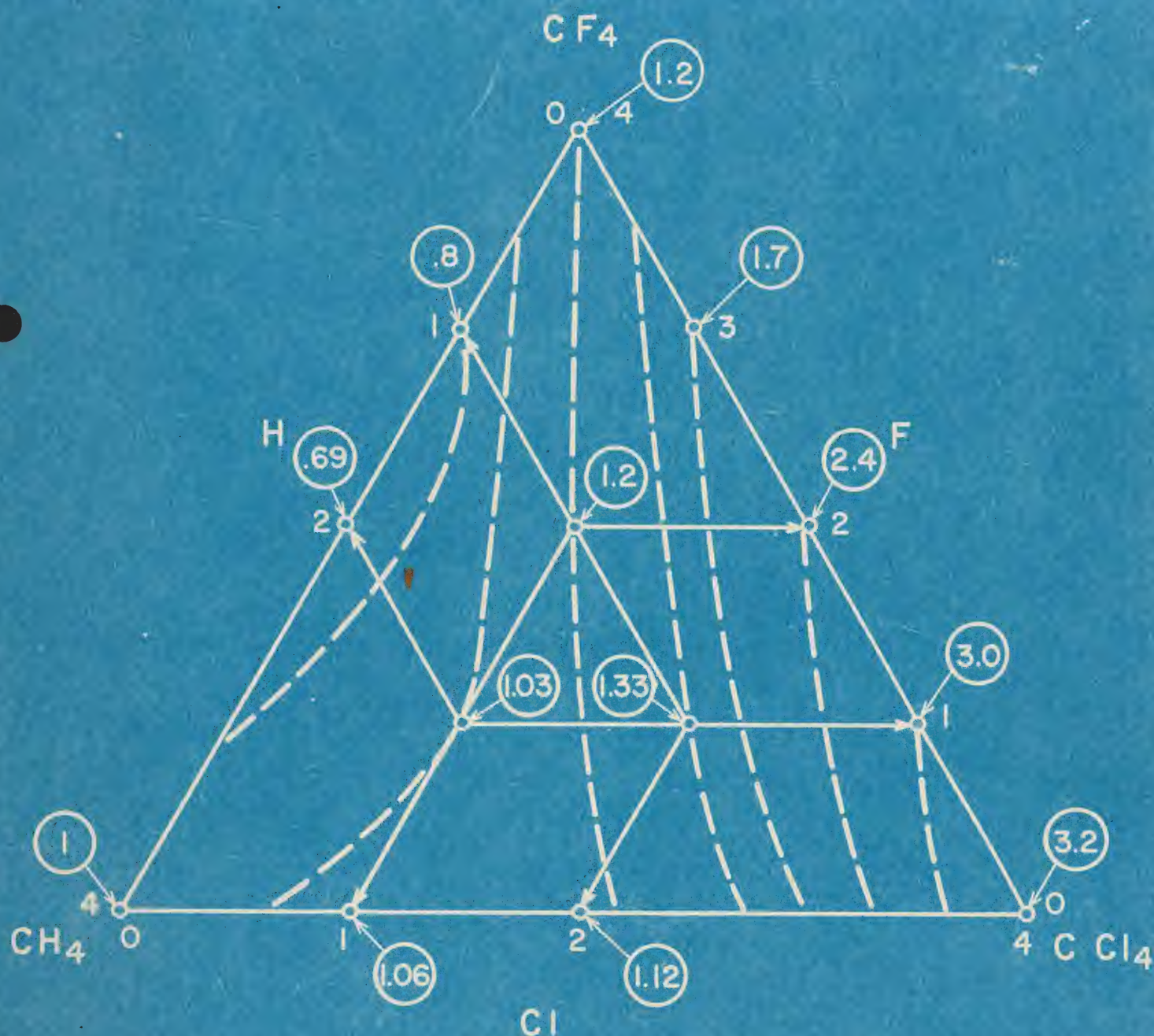


FIG. 3 RELATIVE ELECTRIC STRENGTH (CIRCLED NUMBERS) AS A FUNCTION OF THE NUMBER OF H, F, AND Cl IN METHANE (DASHED LINES INDICATE EQUAL STRENGTH)

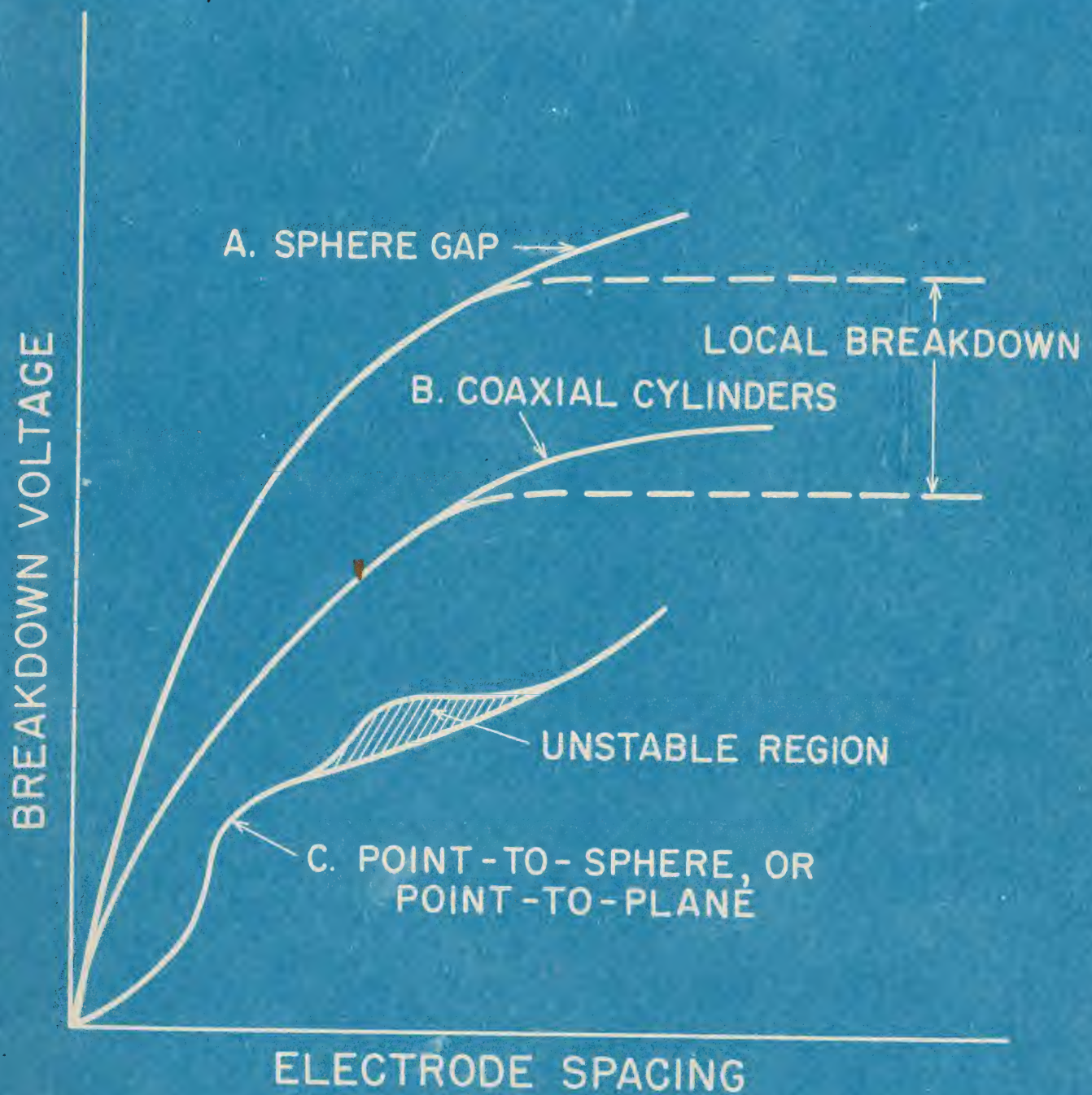


FIG. 4 BREAKDOWN CHARACTERISTICS OF AIR IN NON-UNIFORM FIELDS

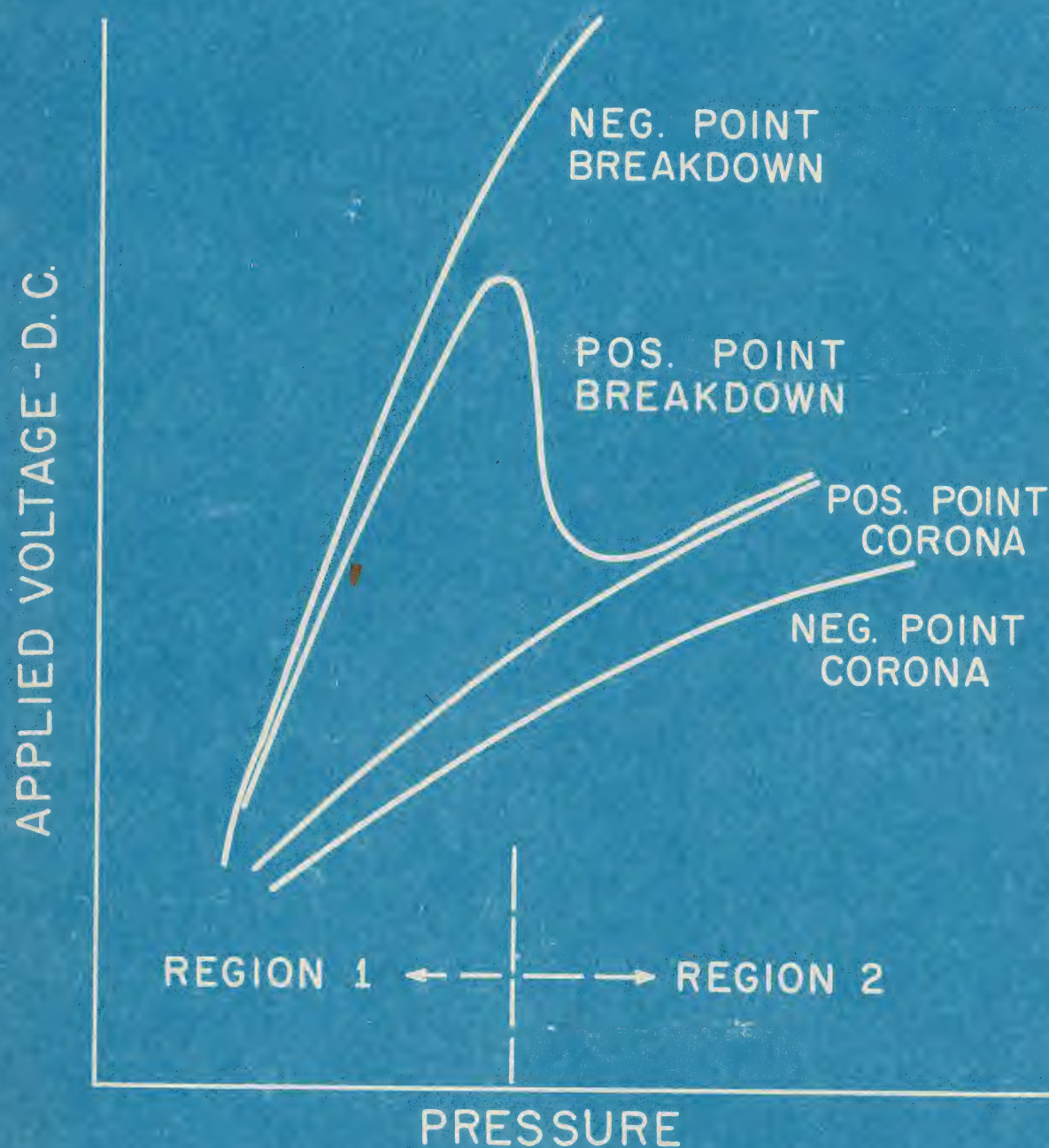


FIG. 5 BREAKDOWN CHARACTERISTICS OF ELECTRO-NEGATIVE GASES IN A POINT-TO- PLANE GAP

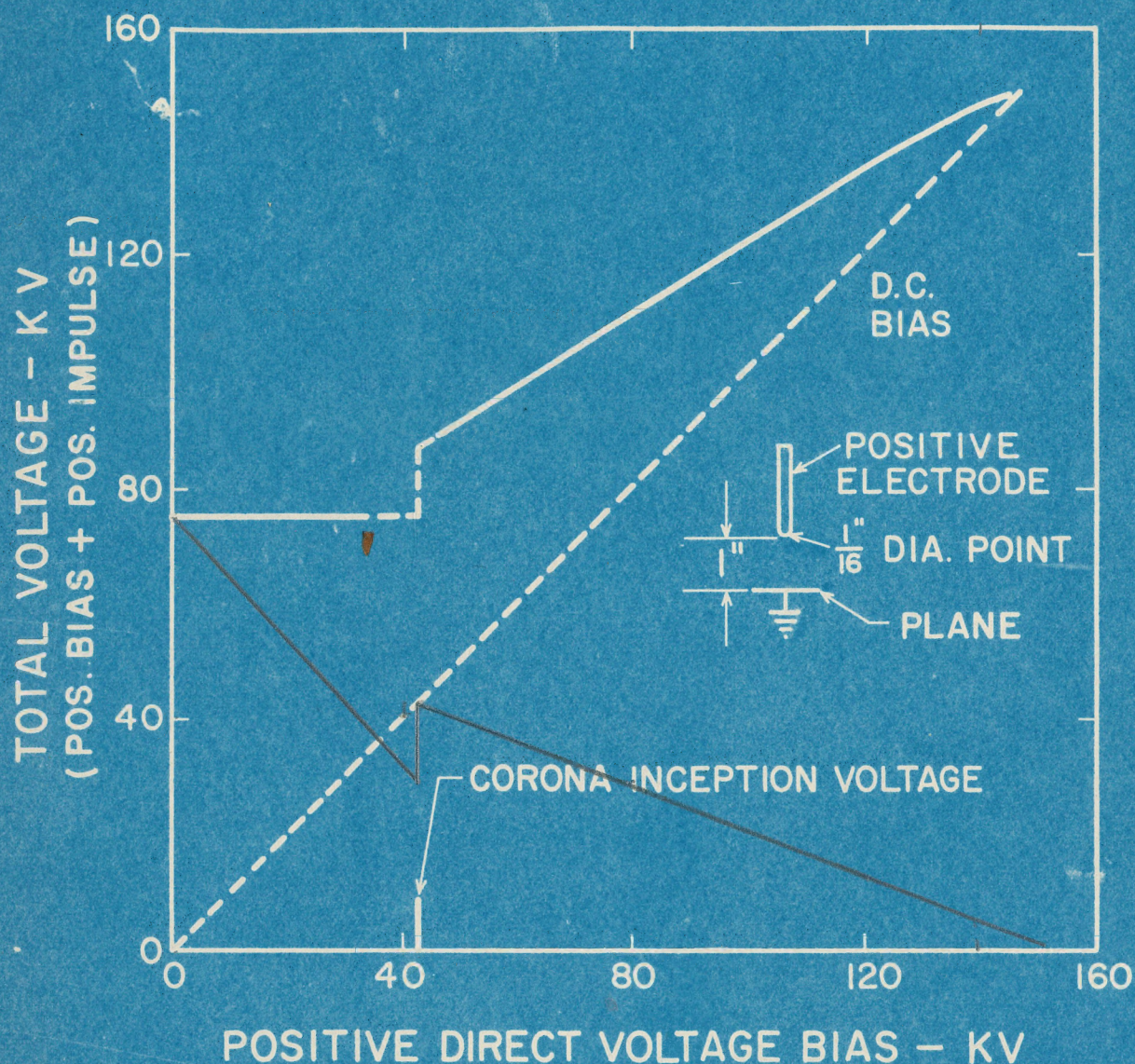


FIG. 6 IMPULSE BREAKDOWN CHARACTERISTICS OF SF_6 IN A NON-UNIFORM FIELD ILLUSTRATING THE EFFECT OF SPACE CHARGE PRODUCED BY POSITIVE D.C. BIAS

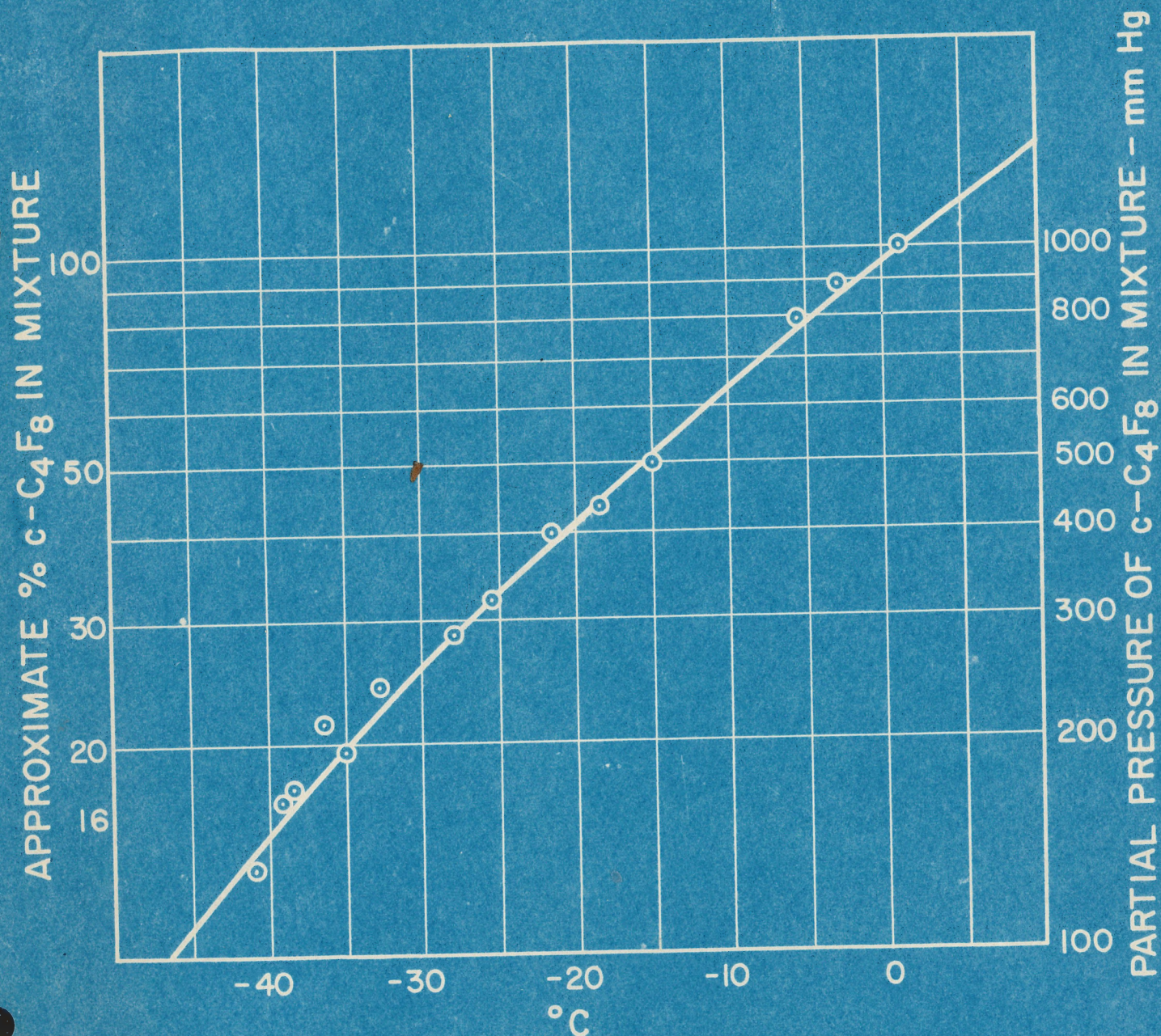
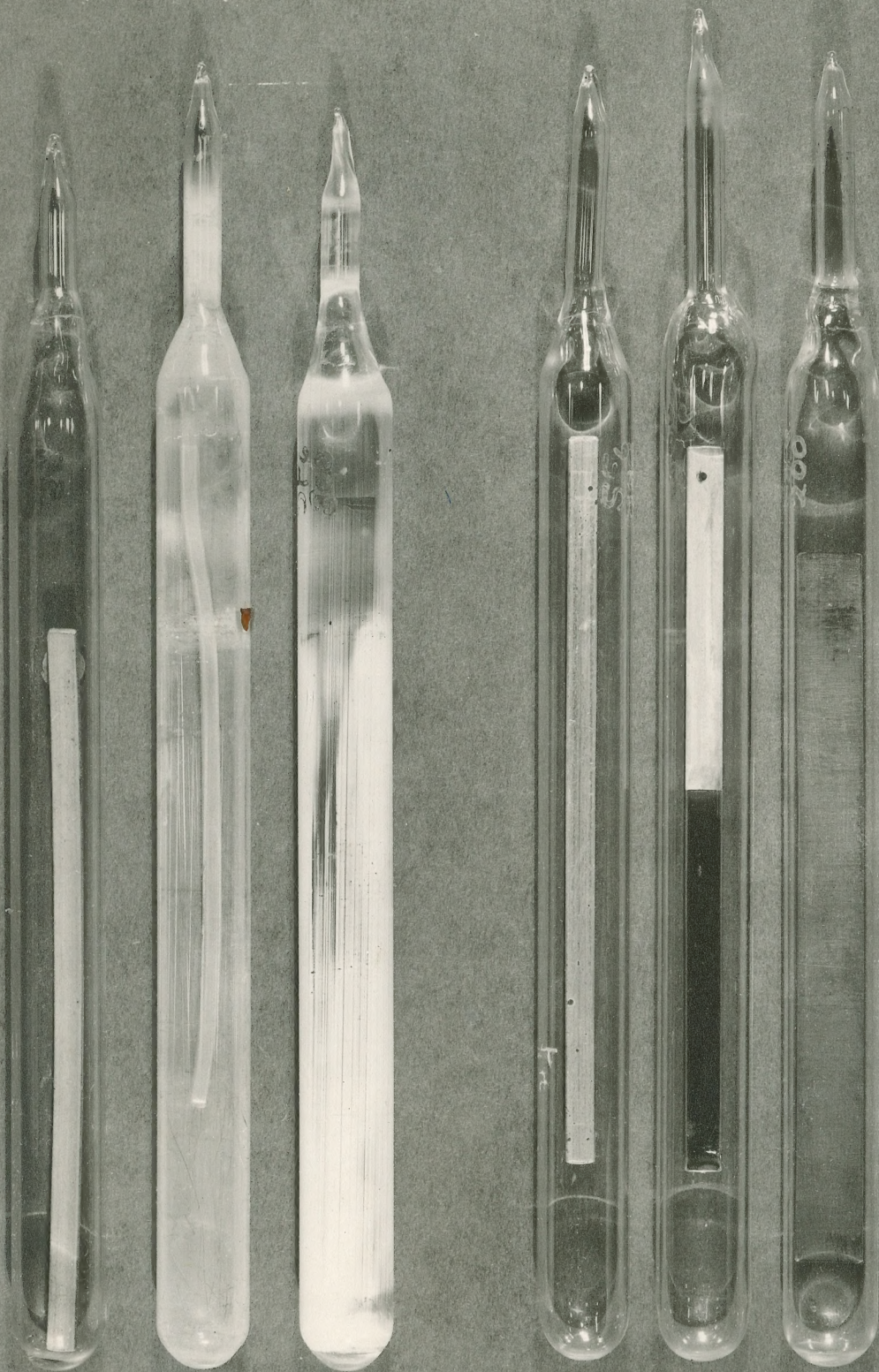


FIG. 8 "DEW-POINTS" OF c-C₄F₈ IN DRY AIR VARYING COMPOSITION AND PRESSURE



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